

In situ Rheological Characterization of Poly(Dimethylsiloxane)-Containing Sol-Gel Protective Coatings

Lidija Slemenik Perše¹, Mirjana Rodošek¹, Darja Merl Kek², Angela Šurca Vuk¹

¹ National Institute of Chemistry, Ljubljana, Slovenia

² Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

ABSTRACT

In situ rheological study of sol-gel process was performed with 3-glycidoxypropyl-terminated polydimethylsiloxane based sols. A continuous following of rheological properties enabled a precise insight in gelation process resulting in exact prediction of gelation time, structural changes and final rheological properties of formed gel. Moreover, as polyhedral oligomeric silsesquioxanes (POSS) are successfully used compounds for improvement of various polymer properties, the influence of POSS on rheological properties, combined with the impact on thermal behaviour and electrochemical properties was studied.

INTRODUCTION

Due to high financial impact (over 4 % on global GDP¹) of corrosion damage, a great research area has been devoted to advanced protective coatings for various metals/alloys. One of the promising are sol-gel protective coatings on the base of poly(dimethylsiloxane), which have been extensively studied in our laboratory²⁻⁴. Recently we reported on the influence of POSS content on the protective properties and structure of coatings, which was evaluated using a potentiodynamic polarisation technique and *ex-situ* IR reflection-absorption (RA) and *in-situ* Raman spectroelectrochemistry⁴. In the

present work we likewise examined epoxypropoxypropyl-terminated poly-(dimethylsiloxane) (EP-PDMS-EP) that requires the application of an amino-crosslinkers, which were introduced as an organic-inorganic hybrid (3-aminopropyl)trimethoxysilane (APTMS) and polyhedral oligomeric silsesquioxane (POSS). The latter could be through amino group bound into the structure of the coating as pendant groups. POSS compounds are characterised by the regular structure of nano-dimensions and represent the smallest silica particles. They are well known for their positive influence on the mechanical hardness, thermal stability, chemical and scratch resistance⁵.

Sol-gel coatings follow the process of transition from liquid to solid, which represents a change in molecular mobility of the polymer matrix. During the transition initial sol with (usually) Newtonian character changes to viscoelastic gel which exhibits altered mechanical and rheological properties. A continuous (*in situ*) study of rheological behaviour during this transition (sol-gel process) can therefore give precise insight in gelation process, i.e. changes in rheological properties. As a result an exact prediction of gelation time, structural changes and rheological properties of formed gel can be determined. The proper balance between elastic and viscous contribution of the sol prior to the

deposition is particularly important in order to achieve the best barrier efficiency tested by electrochemical techniques. Accordingly, the application of the coating on the substrate has to be performed at precise time of gelation process.

As already mentioned, in the present study the sol-gel process of hydrophobic protective coatings for AA 2024 alloy was studied with EP-PDMS-EP with epoxy groups on both sides of the precursor and APTMS and POSS as amino moieties. In order to determine the most appropriate time for the deposition of protective coatings, sol-gel process was followed *in situ* by rheological measurements in linear viscoelastic range. The results were combined with thermogravimetric (TG) and electrochemical impedance spectroscopy (EIS) measurements.

EXPERIMENTAL

Preparation of the sols and deposition of the coatings

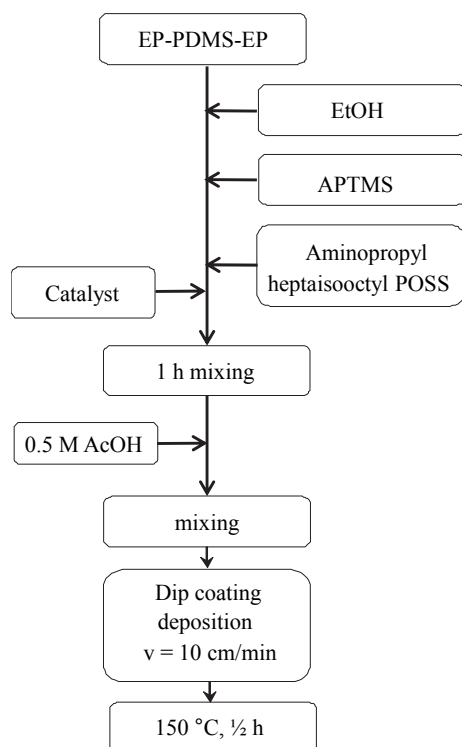


Figure 1. Schematic presentation of the preparation procedure of EP-POSS coatings.

The procedure for the preparation of the coatings is depicted in Fig.1. The first step, where EP-PDMS-EP was dissolved in ethanol, was followed by introduction of APTMS, aminopropyl heptaisooctyl POSS and catalyst of epoxyring opening. During stirring, the sol-gel catalyst, i.e. 0.5 M acetic acid (AcOH), was added into the mixture. The coatings were deposited on the substrate after mixing by dip-coating deposition technique. Time of mixing prior to the deposition depended on the gelation time of the coating, which was determined by rheological tests. After the deposition the coatings were thermally treated at 150 °C for 30 min.

Rheological measurements

Rheological characterization was performed with controlled rate rheometer Physica MCR 301 (Anton Paar) equipped with a parallel-plate geometry sensor system (PP25/1). Standard rotational flow tests were performed with a triangular method by changing shear rate from 0 – 1000 – 0 s⁻¹. Oscillatory stress sweep tests at constant frequency of oscillation (1Hz) were used in order to determine the linear viscoelastic range (LVR). Frequency tests were performed at constant small deformation in LVR by decreasing the frequency from 20 – 0.01 Hz.

The transition from sol to gel was followed continuously through small amplitude oscillatory tests (in LVR) at constant frequency of oscillation ($\omega = 1$ Hz). In order to avoid solvent evaporation during gelation process the sensor system was protected with a special cover. The temperature of all measurements was kept constant at 23°C.

Thermogravimetric measurements

TG measurements were performed on a Netzsch STA 449 (Selb, Germany) thermal analysis system under air conditions. The samples were heated from room temperature up to 700 °C at a heating rate of 10 °C/min.

The xerogels for thermal analyses were prepared by drying a thin layer of sol under ambient conditions for a week and then grounded in a mortar.

Electrochemical Impedance Spectroscopy (EIS) measurements

An Autolab PGSTAT302N potentiostat-galvanostat with FRA module was used to perform Electrochemical Impedance Spectroscopy (EIS) in a K0235 flat cell (Princeton Applied Research) filled with 0.5 M NaCl electrolyte. The coating on AA 2024 was mounted as the working electrode, the counter electrode was the Pt grid and the reference electrode Ag/AgCl/KCl_{sat}. The frequency range used was from 105 to 0.01 Hz. The impedance spectra were measured up to 7 days and all these time the coatings were immersed in 0.5 M NaCl electrolyte.

RESULTS AND DISCUSSIONS

TG measurements

As POSS molecules are often considered as additives that positively influence thermal stability of nanocomposites^{6,7} we analysed the influence of POSS addition on thermal properties of EP-POSS xerogels. TG analysis (Fig. 2) confirmed that the increasing content of added POSS shifted the weight loss onset to higher temperatures, i.e. from 240 to 300 °C, followed by a continuous two-step weight loss up to 600 °C (Fig. 2). Residues at the end of analysis at 700 °C were for the sample without POSS (0.0 POSS) in the range of 45 %, while the values for the samples with the addition of POSS were higher. The results clearly indicate that the thermal stability of prepared xerogels progressively increased with the increase of POSS content.

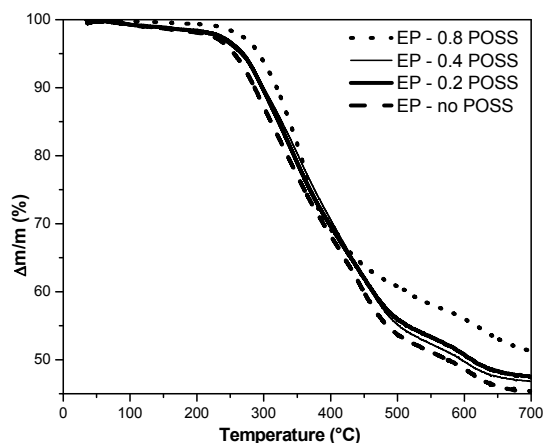


Figure 2. TG curves of EP-POSS xerogels prepared with different content of POSS.

Rheological measurements

As mentioned before, the influence of POSS on sol-gel process and mechanical properties of formed gels were followed *in situ* with rheological oscillatory measurements in linear viscoelastic range (Fig. 3). The addition of POSS clearly prolonged the time of gelation process, as the final gels with solid like rheological properties ($\delta \sim 0^\circ$) were formed at longer times when more POSS was added to the samples. Gelation times were determined from the dependence of δ vs. time at $\delta = 45^\circ$ (Fig. 3B). When no POSS was added, the gelation time was determined at 67 min⁻¹, while for a 0.2 POSS addition the gel point was at 96 min⁻¹, 0.4 POSS at 142 min⁻¹, and at the highest amount of POSS (0.8 POSS) the time needed for the solution to form a gel structure was evaluated at 224 min⁻¹. The sol-gel process of all samples started with similar values of the viscosity and phase shift angle $\delta = 90^\circ$, while at the end of gelation process the viscosity of all samples increased for almost 5 orders of magnitude, while phase shift angle dropped to the values close to 0° . However, the sample with the highest amount of added POSS (EP – 0.8 POSS) exhibited slightly different values of the viscosity and phase angle at the end of gelation process. Compared to

other three formed gels the value of the viscosity for EP-0.8 POSS was one order of magnitude lower (Fig. 3A); while the phase shift angle δ was slightly higher ($\delta < 10^\circ$, Fig. 3B). We can conclude that the addition of POSS had several impacts on rheological properties. Higher amount of POSS (i) prolonged the time of gelation; (ii) decreased final viscosity and (iii) increased phase shift angle of formed gel.

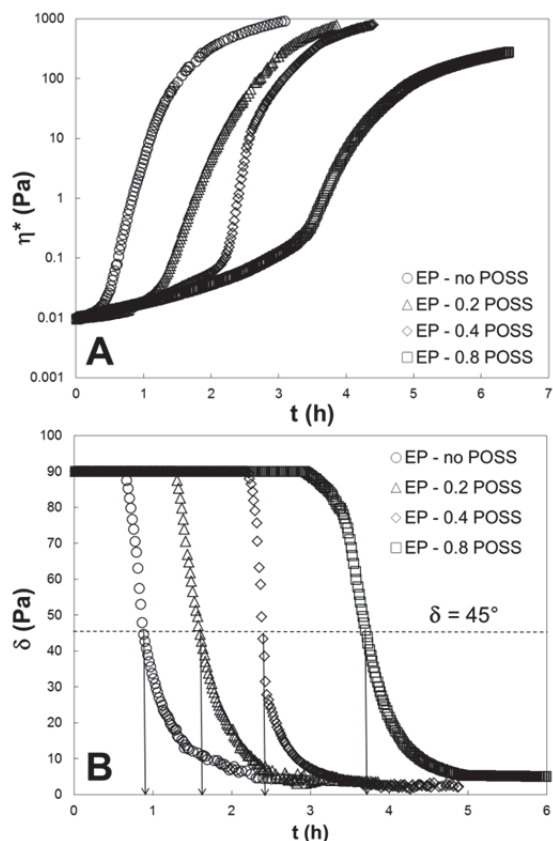


Figure 3. *In situ* rheological measurements in linear viscoelastic range: A) complex viscosity and B) phase shift angle during sol-gel process.

After the gelation process was finished oscillation frequency tests were performed for the formed gels (Fig. 4). The results showed that POSS addition didn't change frequency dependence of viscosity; however the values of the viscosity decreased with increasing amount of added POSS. Nevertheless, negligible effect of POSS addition was observed for the samples with

0.2 and 0.4 POSS, while 0.8 POSS decreased the viscosity for almost two orders of magnitude compared to the sample without POSS addition. Similar negligible effect of POSS addition between the samples EP - 0.2 POSS and EP - 0.4 POSS was observed also with TG measurements (Fig. 2), where the highest impact was also observed between initial sample and the sample with the highest amount of POSS.

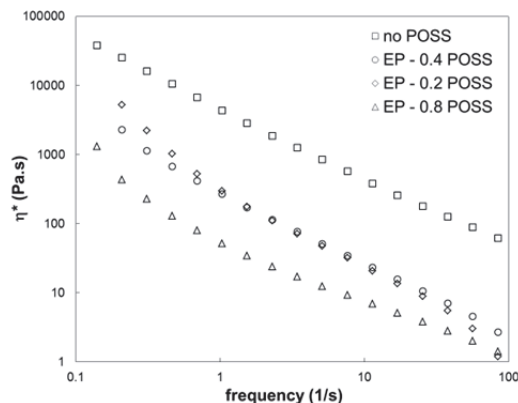


Figure 4. The dependence of complex viscosity on frequency of oscillation for formed gels with different amount of POSS.

For all the samples (with and without POSS) the oscillation frequency tests in the range of linear viscoelastic response were performed also *ex situ* at different times during the gelation process. Similar results were observed for all samples, but for the sake of clarity only the results for EP - 0.2 POSS are presented in Fig. 5. At the beginning, the initial sol exhibited low values of loss modulus G'' , which exhibited strong frequency dependence, while the values of storage modulus were negligible. Newtonian initial sol changed to viscoelastic “liquid-like” already after 1 hour, when storage modulus G' became significant and slightly lower than loss modulus G'' . As gelation proceeded the values of the moduli further increased and their dependences on the frequency changed. 1.5 h after the beginning of solvolysis, G' equalled G'' , and both moduli depended on the frequency of oscillation by the order of 0.5. Such weak

gel behaviour indicated the transition from sol to gel. Weak gels resemble strong gels in their mechanical behaviour, particularly at low frequencies, but as the deformation increases, their networks undergo a progressive breakdown into smaller clusters. As a consequence, the system can flow with flow properties typical of a disperse system.⁸ Formed gels at the end of gelation process exhibited “solid-like” behaviour with much higher values of storage modulus G' compared to the loss modulus G'' ; moreover, the moduli were frequency independent, i.e. $G' \sim \omega^0$. Such behaviour is characteristic for strong gels,⁹ Under the conditions of small deformation, strong gels manifest the typical behaviour of viscoelastic solids and, above a critical deformation values, they rupture rather than flow.⁷ For the sample without POSS (Fig. 3) the transition from sol to gel was completed in 3 h, while for the samples with POSS the structure of strong gel was observed after 3.5 h (for EP – 0.2 POSS), 3.8 h (for EP – 0.4 POSS) and 5 h (for EP – 0.8 POSS) (Fig. 3). We can conclude that the addition of POSS prolonged the time of gelation due to its cube-like appearance, which disturbed the arrangement of linear EP-PDMS-EP and APTMS precursors.

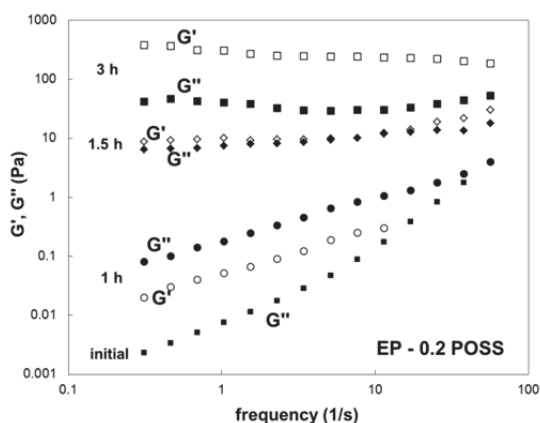


Figure 5. The dependence of dynamic moduli G' and G'' on frequency of oscillation for EP – 0.2 POSS at different times from the beginning of the gelation.

Electrochemical Impedance Spectroscopy

EIS technique was used with the aim to electrochemically test the barrier properties of the prepared EP-POSS coatings. The open-circuit impedances of coatings with and without the addition of POSS were traced over 168 h during the immersion into the 0.5 M NaCl solution and compared to the response of bare AA 2024 substrate (Fig. 6). An excellent anticorrosion coating would typically result in a gradual increase in the impedance with decreasing frequency¹⁰. In the above Bode diagrams, in general, three distinctive segments can be noted in the $\log |Z|$ vs. $\log \nu$ curves (ν is frequency in Hz, Z is impedance) (Fig. 6A-C). In the higher frequency region (up to $\nu = 103$ Hz), $|Z|$ was about $11 \Omega\text{cm}^2$ for AA 2024 (Fig. 6A) and the phase angle tended toward 0° (Fig. 6D). This indicated that only solution resistance was detected up to this frequency region for AA 2024. In contrast, both types of coatings (Figs. 6B,C) were characterised with almost a linear relationship between $\log |Z|$ vs. $\log \nu$ (with a slope close to -1) and with the phase angle approaching -90° (Fig. 6D). This behaviour is typical of a capacitor and is ascribed to the capacitive behaviour of coatings.

In the middle frequency region ($\nu = 10^3$ to 1 Hz), changes in the curves of AA 2024 substrate (Fig. 6A), together with the peak in phase angle diagram (Fig. 6D), resulted from the capacitance of the oxide layer that formed on the aluminium alloy surface^{10,11}. The low-frequency region, in contrast, reflected the processes associated with general corrosion. The $|Z|$ was between 104 and $105 \Omega\text{cm}^2$ for AA 2024. It could be seen that the low-frequency impedances for both kinds of coatings (Figs. 6B,C) are at the beginning of exposure to electrolyte of about 2-3 orders of magnitude larger compared to the bare AA 2024 alloy (Fig. 6A).

With increasing time of exposure, the low-frequency impedance of the coating

without POSS (Fig. 6B) decreased to about $105 \Omega\text{cm}^2$, a value close to bare AA 2024, while the impedance of EP-0.2 POSS (Fig. 6C) remained close to the initial value of $4.5 \times 10^6 \Omega\text{cm}^2$. This clearly indicated the higher corrosion effectiveness of coatings with added POSS. Moreover, the addition of POSS stabilised the shape of the impedance spectra in the whole frequency region, and consequently, the anticorrosion ability of the coatings. The Bode diagrams for recently prepared similar polyurethane-POSS systems, however, showed initial impedance values from 108 to $109 \Omega\text{cm}^2$, depending on the number of deposited layers (5 to $20 \mu\text{m}$) and the content of POSS¹⁰. Prolonged immersion time led to a decline of the high and middle frequency resistive region in the $\log |Z|$ vs. $\log \nu$ spectrum for the coating without POSS (Fig. 6B) that was almost linear. This suggested that the capacitive and resistive properties of the coating differed as a result of the electrolyte penetration through coating, as has been discussed previously¹².

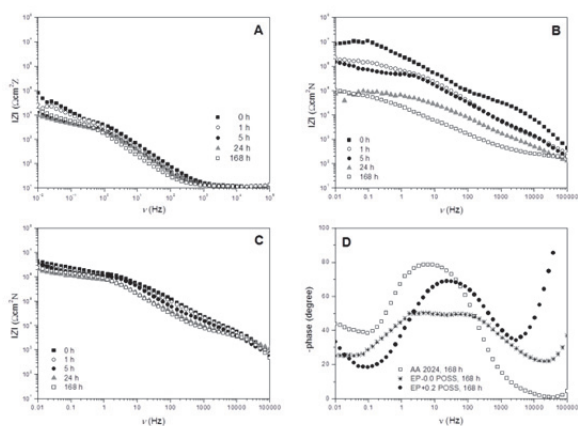


Figure 6. Bode curves of: A) bare AA 2024 alloy, B) EP-0.0 POSS and C) EP-0.2 POSS coatings and D) phase angles plot.

CONCLUSIONS

A systematic rheological, thermogravimetric and EIS study of protective coatings on the base of

epoxypropoxypropyl-terminated poly-(dimethylsiloxane) with and without POSS clearly demonstrated the increased barrier efficiency and thermal stability with the addition of POSS. Formed gel with no POSS addition exhibited viscoelastic solid-like and brittle gel structure with high elastic modulus G' and negligible viscous contribution G'' . In contrast, the addition of POSS led to the formation of gels with considerable viscous contribution G'' . The results of rheological measurements showed that POSS (i) increase the time of gelation, (ii) decrease complex viscosity of formed gels and (iii) enable the formation of gel structures with significant viscous G'' and elastic G' modulus resulting in softer gel structure. Results demonstrated that the coatings with such rheological properties exhibit higher corrosion effectiveness and higher thermal stability.

ACKNOWLEDGMENTS

This work was financed by the Slovenian Research Agency (Programme P1-0030 and Project L2-5484). M. Rodošek acknowledges the Slovenian Research Agency for her Ph.D. grant.

REFERENCES

1. Wang, D. and Bierwagen, G.R. (2009), "Sol-gel coatings on metals for corrosion protection", *Prog. Org. Coat.*, **64**, 327-338.
2. Fir, M., Orel, B., Šurca Vuk, A., Vilčnik, A., Ješe, R., Francetič R. (2007), "Corrosion studies and interfacial bonding of urea/poly(dimethylsiloxane) sol/gel hydrophobic coatings on AA 2024 aluminum alloy", *Langmuir*, **23**, 5505–5514.
3. Rauter, A., Slemenik Perše, L., Orel, B., Bengu, B., Sunetci, O., Vuk Šurca, A., (2013), "Ex situ IR and Raman spectroscopy as a tool for studying the anticorrosion processes in (3-glycidoxypropyl)-trimethoxysilane-based sol-gel coatings, *J. Electroanal. Chem.*, **703**, 97–107.

4. Rodošek, M., Rauter, A., Slemenik Perse L., Merl Kek, D., Surca Vuk, A. (2014), "Vibrational and corrosion properties of poly(dimethylsiloxane)-based protective coatings for AA 2024 modified with nanosized polyhedral oligomeric silsesquioxane", *Corr. Sci.*, **85**, 193-203.
5. Sun, D.Z., Hu, L.J., Zhang, X.W., Lu, Z.S. (2008) "Nanostructures and properties of hybrid films based on DGEBA and modified with APES/PGE polyhedral oligomeric silsesquioxanes", *Colloid Surface A*, **313**, 278–281.
6. Zhao, Y. and Schiraldi, D. A. (2005) "Thermal and mechanical properties of polyhedral oligomeric silsesquioxane (POSS)/polycarbonate composites", *Polymer*, **46**, 11640–11647.
7. Fina, A., Tabuani, D., Carniato, F., Frache, A., Boccaleri, E. and Camino, G., (2006), "Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation", *Thermochim. Acta*, **440**, 36-42.
8. Lapasin, R. and Pricl, S. (1995), "Rheology of Industrial Polysaccharides: Theory and Applications" Blackie Academic & Professional, London.
9. Larson, R. G. (1999), "The structure and Rheology of Complex Fluids", Oxford University Press, New York.
10. Markevicius, G., Chaudhuri, S., Bajracharya, C., Rastogi, R., Xiao, J., Burnett, C., Chastek, T.Q. (2012), "Polyoligomeric silsesquioxane (POSS)-hydrogenated polybutadiene polyurethane coatings for corrosion inhibition of AA2024", *Prog. Org. Coat.*, **75**, 319-327.
11. Kek Merl, D., Panjan, P., Kovač, J. (2013), "Corrosion and surface study of sputtered Al-W coatings with a range of tungsten contents", *Corros. Sci.*, **69**, 359-368.
12. Perez, C., Collazo, A., Izquierdo, M., Merino, P., Novoa, X.R. (1999), "Characterisation of the barrier properties of different paint systems - Part I. Experimental set-up and ideal Fickian diffusion", *Prog. Org. Coat.*, **36**, 102-108.